NICKEL BASE HEAT RESISTANT CAST ALLOY AND TURBINE WHEELS MADE THEREOF

BACKGROUND OF THE INVENTION

Field in the Industry

The present invention concerns a nickel base heat resistant cast alloy and turbine wheels made from the alloy for automobile engines. The invention provides turbine wheels having the strength higher than that of the conventional ones with substantially the same cost.

Prior Art

Because turbine wheels for automobile engines are the parts subjected directly to high-temperature exhaust gas, requirements for heat resistant property and enough strength at high temperature thereof are severe. To date, as the material for turbine wheels of ordinary passenger cars INCONEL 713C (hereinafter abbreviated as "713C") has been used. The alloy has a long history of practical use (Japanese Patent Publication Sho.42[1967]-11915). On the other hand, as the material for the turbine wheels used under severer conditions, such as for engines of rally cars, there has been used Mar-M 247 (hereinafter abbreviated as "MM-247") having the strength higher than that of

713C. This alloy also has been known and used for many years (Japanese Patent Disclosure Sho.47[1972]-13204).

While it is anticipated that exhaust gas temperature will be much higher in the near future due to increase of output of passenger car engines, 713C may not meet the demand due to its insufficient high temperature strength. On the other hand, MM-247 contains hafnium, which is expensive, as one of the components of this alloy and the material cost is thus high. Moreover, HIP process is often used at manufacturing the wheels so that voids may not occur in the cast products and therefore, manufacturing cost is high.

The efforts for solving these problems have been continued for years and resulted in proposing turbine wheels made of nickel base heat resistant cast alloy which achieved the creep rapture strength higher than that of 713C (Japanese Patent Disclosure Hei.11[1998]-131162 and 2000-169924). These materials have, however, alloy compositions comprising niobium (the former contains 0.5-3.5% and the latter, 6.0-8.0%), which brought about a new problem of easy segregation of Nb. Furthermore, these alloys contain molybdenum (both 1.0-5.0%) and therefore, high temperature oxidation resistance is not so high. As the conclusion, from the viewpoints of balanced cost-saving and merits of improvement, it cannot be said

that fully satisfactory, low-cost Ni-base heat resistant cast alloy have been developed.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a nickel-base heat resistant cast alloy used as the material for turbine wheels of automobile engines having the high strength at high temperature to meet the tendency of increasing exhaust gas temperature, and with respect to the material cost, though a little higher, with substantially the same cost, while the heat resistance property and the high temperature strength are about the same as those of MM-247. To provide turbine wheels made of this material is also the object of this invention.

The nickel base heat resistant cast alloy of the invention consists essentially of, by weight %, C: 0.02-0.50%, Si: up to 1.0%, Mn: up to 1.0%, Cr: 4.0-10.0%, Al: 2.0-8.0%, Co: up to 15.0%, W: 8.0-16.0%, Ta: 2.0-8.0%, Ti: up to 3.0%, Zr: 0.001-0.200% and B: 0.005-0.300% and the balance of Ni and inevitable impurities, provided that [%Al]+[%Ti]+[%Ta], by atomic %, amounts to 12.0-15.5%, that it contains γ/γ'-eutectoid of, by area percantage, 1-15%, that it contains carbides of, by area percentage, 1-10%, and that the "M-value" defined by the formula below (in which % is atomic %) is in the range of 93-98:

$$M=0.717[\%Ni]+1.142[\%Cr]+2.271[\%Ti]+1.9[\%Al]+2.117[\%Nb]+1.55[\%Mo]+0.777[\%Co]+3.02[\%Hf]+2.224[\%Ta]+1.655[\%W]+2.994[\%Zr]$$

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The Ni-base heat resistant cast alloy according to the present invention may contain, in addition to the above mentioned basic alloy components, at least one of the group consisting of Mg: up to 0.01%, Ca: up to 0.01% and REM: up to 0.1%.

The main impurities which may be contained in the present Ni-base heat resistant cast alloy of the invention are Fe, Si, Mn, P and S, originated from the raw materials. Depending on the cases, Cu and Mo may also be contained. It is preferable to regulate the contents of the impurities at highest up to the following respective upper limits:

Fe: up to 5.0%, Mo: 1.0%, Cu: 0.3%, P: 0.03%, S: 0.03%, and V: 1.0%.

The effects of the alloy components and the reasons for limiting the alloy compositions as defined above will be explained below together with the significance of the limitations of the above-mentioned [%Al]+[%Ti]+[%Ta], area percentage of γ/γ'-eutectoid, area percentage of carbides and the "M-value".

C: 0.02-0.50%, preferably 0.05-0.30%, more preferably 0.05-0.20%

Carbon contributes to strengthening of grain boundaries by, in case of an element of the group of Ti, Zr and Hf, or an element of the group of Nb, Ta and V, combining with it to form carbide or carbides thereof. A carbon content less than 0.02% may not give sufficient effect, while a content exceeding 0.50% will cause formation of excess carbide or carbides, which results in decreased corrosion resistance and ductility. Preferable C-content is in the range of 0.05-0.30%, and more preferable range is 0.02-0.20%.

Si: up to 1.0%

Silicon is usually used as a deoxidizing agent at the time of melting and refining the alloy. Though content of a small amount of Si effective as the deoxidizing agent may cause no problem, too much addition will lower the ductility of the alloy. Thus, 1.0% is set as the upper limit. Preferable Si-content is up to 0.5%.

Mn: up to 1.0%

Manganese is, like silicon, also added as a deoxidizing agent. Addition in a small amount effective as the deoxidizing agent may cause no problem, however, too much addition will lower the strength and the ductility of the alloy. The upper limit, 1.0%, is thus set.

Cr: 4.0-10.0%

Chromium is the most important element for

improving the corrosion resistance of the alloy. It also contributes to increase of the strength by solid solution in the matrix phase. Addition amount less than 4.0% will give little effect, while more than 10.0% lowers the phase stability and the strength and the ductility of the turbine wheel after operation at a high temperature for a long period of time. Preferable range of Cr-content is 6.0-10.0%.

Al: 2.0%-8.0%

Aluminum is an important element forming γ'-phase, and is useful for improving high temperature corrosion resistance. These effects may be week at such a small amount as less than 2.0%. On the other hand, addition exceeding 8.0% causes deposition of much amount of eutectic γ'-phase in casting, and as the result, creep rapture strength will decrease. Preferable range of Al-content is 4.5-5.5%.

Co: up to 15.0%

Cobalt strengthens γ-phase by solid solution. It also dissolves in γ'-phase, which is effective for increasing the strength of the alloy, and strengthens the γ'-phase. Co increases deposition amount of the γ-phase. However, because Co is an expensive material, addition in a large amount is disadvantageous from the viewpoints of the cost. Choosing an addition amount up to 15.0% is recommended. In order to ensure sufficient high temperature properties at 900°C or higher, it is desirable to add Co in an amount of 5.0%

or higher.

W: 8.0-16.0%

Wolfram contributes greatly to solution strengthening of the γ-phase and increase of the strength. An amount less than 8.0% will give insufficient effect, while an amount exceeding 16.0% lowers the phase stability. The lowered phase stability causes deposition of α-Cr in the alloy after using for a long while and damages the strength of the wheels. A preferable range of addition is 10.0-14.0%.

Ta: 2.0-8.0%

Tantalum not only combines with carbon to form the carbide, but also dissolves in the γ'-phase to strengthen it. The effect is low at addition amount less than 2.0%. Because Ta is an expensive material like Hf, from the viewpoint of the cost, it is desirable to use it in an amount as small as possible. The upper limit, 8.0%, is thus set.

Ti: up to 3.0%

Titanium reacts Ni to form the γ'-phase which is effective in increasing the strength of the alloy. Ti has further effect of replacing Al to contribute to solution strengthening of the γ'-phase, and thus, further improves the strength of the alloy. However, addition of Ti exceeding 3.0% tends to cause deposition of η-phase (Ni_3Ti), which gives disadvantage to the high temperature strength and the ductility of the alloy. Preferable amount of addition is 2.0% or

less.

Zr: 0.001-0.200%

Zirconium has both the effect of combining with carbon to form the carbide and the effect of segregating at the grain boundaries to strengthen. These effects are observed at even such a small amount of addition as 0.001%. Due to decrease of the ductility at addition of a large amount the upper limit is set to be 0.200%. An optimum amount of addition may be found in a range up to 0.1%.

B: 0.005-0.300%, preferably 0.050-0.200%

Effects of adding B are suppressing formation of the η-phase to prevent decrease of the high temperature strength and the ductility, and further, enhancing the high temperature creep rapture strength. Also, B forms borides with Cr and some other elements. Because melting points of the borides are low, the temperature range of solid-liquid coexisting is board, and thus, castability of the alloy will be improved. To seek these effects, it is necessary to add a suitable amount of B in the range of 0.005% or more. Addition in an excess amount, however, results in decrease of the strength and the ductility of the alloy. Thus, the upper limit of addition is set to 0.300%. Favorable balance of the castability and strength-resilience can be achieved in the range from 0.050 to 0.200%.

One or more of Mg: up to 0.01%, Ca: up to 0.01% and

REM: up to 0.1%

Both Magnesium and calcium segregate at the grain boundaries to strengthen. REM has the same effect. Large amount addition of any element or elements is not advisble due to decrease of the strength and the ductility of the alloy. The upper limits of addition are thus set to be 0.01% for Mg and Ca, and 0.1% for REM.

Regulation on the contents of the impurities to the following upper limits:

Fe: 5.0%, Mo: 1.0%, Cu: 0.3%, P: 0.03%, S: 0.03% and V: 1.0%.

In the case where iron scrap, a cheep raw material, is intended to use for the purpose of decreasing the manufacturing cost, various impurities will come into the product alloy. The element which may get mixed with the highest possibility is Fe, which is harmful to all the properties of the strength, the corrosion resistance at room- and high temperature. Allowable limit of Fe-content is 5.0%, and 3.0% or less is preferable. Phosphor segregates at the grain boudaries to cause lowered strength, and therefore, content of a large amount of P is undesirable. However, it is inevitable that a certain amount exists in the alloy. The allowable limit of P is 0.03%. Sulfur is also an element decreasing the strength like P, and the S-content is preferably limited to be 0.03% or less. Molybdenum, though it dissolves in the

matrix of the alloy to contribute to increasing the strength, content at a large amount damages the high temperature oxidation resistance, and thus, the Mo-content should be such amount as up to 1.0%. Copper is also the cause of decreased strength, and therefore, existence of Cu in a large amount is not desirable. The allowable upper limit is 1.0%, and Cu-content of 0.3% or less is preferable. Vanadium brings about the disadvantage of decreased high temperature strength, and the V-content should be limited to less than the upper limit, 1.0%.

[%Al]+[%Ti]+[%Ta]: 12.0-15.5 atomic %

In order to ensure sufficient strength and workability of the alloy this condition must be met. Outside this range there are the following disadvantages. If the amount is less than 12.0%, the lower limit, then satisfactory strength may not be obtained, and if the amount is more than 15.5%, the upper limit, then cracks tend to occur in the cast products.

Area percentage of γ/γ'-eutectoid: 1-15%

Keeping the lower limit, 1%, is necessary for ensuring the workability, particularly, castability of the alloy. In case where the area percentage is less than 1%, voids may occur at the last stage of casting, and the liability of the product wheels will become low. On the other hand, in case where the area percentage exceeds 15%, the eutectoid may become the

starting points of fracture.

Area percentage of carbides: 1-10%, preferably 1-5%

Formation of a suitable amount of carbides is useful for strengthening the grain boundaries and enhance the high temperature strength at 1000°C or higher. When the area percentage of the carbides is 1% or more, this effect can be obtained, and when the area percentage exceeds 10%, it is lost. Preferable range of the area percentage of the carbides is 1-5%.

M-value: 93-98

The M-value defined by the formula above is a measure for the phase stability. The M-value in the range of 93-98 guaranties the durability of the product turbine wheels. Because the alloy of this invention is used for automobile parts, a higher M-value is advantageous to give longer durability of the parts. However, at an M-value exceeding 98, harmful phases such as σ-phase tend to occur after using for a long period of time, and the durability will decrease.

Though the Ni-base heat resistant cast alloy according to the invention contains no expensive Hf, which is effective for strengthening the alloy, it has creep rapture strength much better than that of 713C alloy which is used most widely as the material for the turbine wheels, and the creep rapture strength of the invented alloy is substantially the same as that of MM-247 containing Hf. Based on the alloy

composition, the material cost may be a little higher than that of 713, but still lower than that of MM-247. Because of high castability of the present alloy HIP process is not necessary to apply, and thus, the cost for manufacturing the turbine wheels may not be high. The present invention thus makes it possible to provide turbine wheels, which can meet the anticipated increase of exhaust gas temperature in the near future, at lower prices.

EXAMPLES

Nickel-base heat resistant alloys having the alloy compositions shown in Table 1 (Working Examples) and Table 2 (Control Examples) were produced and cast into ingots weighing 50kg. No.A of the Control Examples is the conventional 713C alloy, and No.B corresponds to MM-247. Properties of these alloys such as [%Al]+[%Ti]+[%Ta] are shown in Table 3 (Working Examples) and Table 4 (Control Examples). Test pieces were taken from the ingots by machining, and they were subjected to creep rapture tests at the conditions of 1000°C and 180MPa. The determined creep properties are shown in Table 3 and Table 4.

In regard to the alloys of the Working Examples No.8 and No.9 the area percentages of γ/γ'-eutectoid were adjusted to be 3.2% (No.8 and No.9) and 18.5 (No.8A and No.9A) by regulating the cooling rates

after casting. The samples were also subjected to the creep tests of the same conditions, 1000°C and 180MPa. The results are shown in Table 5. For convenience of comparison the data of the case of area percentage 7.1% is shown in Table 5 again.

TABLE 1 Alloy Compositions (Working Examples)

No.	C	Si	Mn	Cr	Co	W	Ta	Al	Ti	Zr	B	Others
1	0.15	0.06	0.08	8.1	11.6	11.9	4.9	5.2	1.1	0.05	0.015	-
2	0.13	0.11	0.07	4.3	9.1	10.3	5.1	5.0	1.0	0.04	0.015	-
3	0.16	0.08	0.06	5.9	-	13.1	4.5	5.2	1.4	0.05	0.013	-
4	0.11	0.07	0.06	7.4	12.2	8.3	4.7	5.3	1.3	0.04	0.020	-
5	0.13	0.12	0.04	9.0	10.9	14.2	2.2	5.6	1.2	0.05	0.018	-
6	0.12	0.42	0.06	7.9	9.2	11.1	7.6	5.1	0.9	0.04	0.016	-
7	0.14	0.14	0.39	7.3	10.0	13.2	5.1	4.1	2.6	0.05	0.015	-
8	0.12	0.08	0.08	6.2	13.6	11.2	3.2	6.8	0.4	0.03	0.011	-
9	0.11	0.07	0.07	6.3	12.8	10.9	7.9	2.1	2.9	0.04	0.013	-
10	0.05	0.13	0.06	8.2	10.4	12.3	4.6	5.3	0.9	0.03	0.013	-
11	0.18	0.12	0.08	9.2	11.4	13.0	4.5	5.2	1.0	0.05	0.014	-
12	0.14	0.12	0.09	7.3	9.1	13.0	4.8	4.9	1.4	0.01	0.015	-
13	0.13	0.10	0.10	8.2	11.2	9.3	4.6	5.1	0.9	0.18	0.012	-
14	0.12	0.13	0.06	9.3	10.9	12.2	4.7	5.4	1.1	0.04	0.006	-
15	0.04	0.12	0.05	8.2	10.1	12.1	4.7	5.3	1.2	0.05	0.14	-
16	0.10	0.14	0.08	8.2	10.1	11.6	4.3	5.2	0.9	0.04	0.003	Mg 0.005
17	0.11	0.11	0.09	8.3	10.6	12.1	4.6	5.3	1.1	0.05	0.002	Ca 0.006
18	0.13	0.09	0.12	8.2	10.1	12.2	4.6	5.3	1.0	0.05	0.056	-
19	0.14	0.10	0.11	8.4	10.9	12.4	4.3	5.2	0.9	0.05	0.260	-
20	0.14	0.12	0.09	7.3	9.1	13.0	4.8	4.9	1.4	0.01	0.058	-

TABLE 2 Alloy Compositions (Control Examples)

No.	C	Si	Mn	Cr	Co	W	Ta	Al	Ti	Zr	B	Others
A	0.15	0.12	0.08	8.3	10.0	10.0	2.9	5.6	1.1	0.05	0.015	Mo 0.7 Hf 1.5
B	0.12	0.12	0.06	12.0	-	-	-	5.9	0.8	0.15	0.015	Mo 4.0 Nb 2.3
C	0.19	0.11	0.08	8.4	9.8	9.8	4.7	5.1	1.2	0.16	0.014	-
D	0.11	0.12	0.06	9.5	14.2	14.2	5.8	5.2	2.9	0.05	0.015	-
E	0.12	0.09	0.08	9.1	9.5	9.5	4.7	5.1	1.0	0.04	0.012	Fe 5.3
F	0.10	0.12	0.09	8.6	10.3	10.3	4.5	5.2	1.1	0.05	0.012	S 0.1

TABLE 3 Results (Working Examples)

No.	Ti+Al+Ta (atomic %)	γ/γ'-Eutectoid (area percentage)	Carbide (area percentage)	M-value	Creep Property Life(hr)	Creep Property Elongation
1	12.58	3.9	4.2	94	47	3
2	12.28	2.5	3.8	92	45	4
3	12.45	3.3	4.1	93	48	3
4	12.19	2.0	4.7	94	44	3
5	12.73	4.1	4.3	95	45	4
6	12.89	4.6	4.2	94	44	5
7	12.21	2.7	3.9	94	45	3
8	14.33	12.2	4.0	95	47	4
9	12.16	2.1	4.5	94	42	6
10	12.25	2.4	1.3	93	41	7
11	12.29	2.6	4.2	94	45	4
12	12.30	2.7	3.7	94	43	3
13	12.19	2.5	3.8	93	48	4
14	12.86	9.2	3.6	95	47	4
15	12.76	3.6	1.1	94	43	5
16	12.22	2.7	4.2	94	46	4
17	12.67	3.1	4.4	94	45	4
18	12.52	4.0	4.7	94	52	6
19	12.03	3.9	4.9	94	46	7
20	12.30	2.7	37	94	48	6

TABLE 4 Results (Control Examples)

No.	Ti+Al+Ta (atomic %)	γ/γ'-Eutectoid (area percentage)	Carbide (area percentage)	M-value	Creep Property Life(hr)	Creep Property Elongation
A	13.61	8.5	4.7	96	46	3
B	13.63	3.2	3.2	96	14	11
C	12.30	7.3	5.7	95	32	2
D	14.52	6.2	3.9	99	36	4
E	12.15	1.9	4.0	96	34	5
F	12.40	2.3	4.2	95	38	4

TABLE 5

No.	γ/γ'-Eutectoid (area percentage)	Creep Property Life(hr)	Creep Property Elongation
8	12.2	47	4
8A	18.1	36	10
9	2.1	42	6
9A	0.4	Many casting defects occurred.	